Jpn. J. Appl. Phys. Vol. 38 (1999) pp. 3841–3844
Part 1, No. 6B, June 1999

Si(111) Surface under Phase Transitions Studied by the Analysis of Inner Layer Structures Using Bias-Dependent Scanning Tunneling Microscopy

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(Received February 15, 1999; accepted for publication April 5, 1999)

In both cases of quenched and HBO_2-molecule-irradiated Si(111) surfaces, corner holes are observed to exist along the boundaries between 7×7 and disordered structural domains. From the analysis of the bias-dependent STM images, it was found that the corner holes included complete stacking fault and dimer structures in the second layer, i.e., a complete corner hole. This result strongly indicates that the complete corner holes play important roles in both the formation and stabilization processes of the dimer-adatom-stacking fault (DAS) structure. In addition, the formation of a structure similar to that of the corner hole was often observed at the boundaries of three out-of-phase c(2×8) structural domains in quenched surfaces, which may result in nucleuses for the formation of the complete corner hole.

KEYWORDS: complete corner hole, Si(111), underlying layer structure, quench, HBO_2

1. Introduction

The Si(111)-7×7 reconstructed surface has been extensively studied, and the dimer-adatom-stacking fault (DAS) model proposed by Takayanagi *et al.*[1)] is widely accepted for explaining the structure. The DAS structure consists of three atomic layers, i.e., the adatom, stacking fault, and dimer layers. The atomic and electronic structures of the 7×7 reconstructed surface in the static form have been discussed extensively, and in most part have been clarified. However, the dynamic mechanism behind the formation and stabilization processes of the DAS structure still remains unsolved, because of the complicated reconstruction involving the first few surface layers.

In order to clarify these processes, quenched and molecule-adsorbed Si(111) surfaces have been analyzed using scanning tunneling microscopy (STM).[2–7)] In the case of the quenched Si(111) surface, the high-temperature "1×1" phase is frozen during the rapid cooling process. Therefore, the analysis of the quenched surface yields information about the formation process of the DAS structure. On the other hand, in the case of the molecule-adsorbed Si(111) surface, STM images show the destruction process of the 7×7 structure induced by the foreign molecules and yield information about the stability of the DAS structure.

Recent high-temperature STM studies of quenched surfaces revealed that the growth of DAS domains occurred with a single faulted half unit as the building unit and faulted half units were formed sharing corner holes.[2–4)] At the boundaries between 7×7 and disordered domains, intrusion of the faulted half units into the disordered region was also observed from the corner holes.[5,6)] Furthermore, in the destruction process of the DAS structure, corner holes remained at the boundaries between the 7×7 and disordered structures.[7)] These results strongly suggest that corner holes play important roles in both the formation and stabilization processes of the DAS structures.

Some analyses have been carried out within the framework of the role of corner hole.[7)] However, only the atomic structure of the topmost adatom layer was analyzed in previous studies, in spite of the fact that the information on the atomic arrangement in the second and third layers is important for the understanding of the formation and stabilization processes of the DAS structures in detail. The lack of information about the underlying layers is mainly due to the fact that STM images generally yield information only about the topmost layer. Therefore, in order to clarify the role of corner holes in detail, it is necessary and important to analyze the underlying layer structures of corner holes.

It is well known that the DAS structure has a characteristic electronic property; charge transfer from the top-layer adatoms to rest atoms in the underlying layer. The amount of the charge transfer from adatoms to rest atoms depends on the number of rest atoms which surround the adatoms.[8,9)] This characteristic electronic property makes it possible to analyze the atomic arrangement in the second and third layers of the DAS structure. The structure of underlying layers can be discussed by considering the redistribution of charge density on adatoms in STM images at negative sample bias voltages.[10,11)] In fact, we recently succeeded in analyzing the structures of the 7×7 phase boundaries by studying the bias-dependent STM images.[10)] In consideration of the characteristic electronic property of the DAS structure described above, the observed charge redistribution on the top layer could be comprehensively related to the structural change in the dimer layer caused by the phase mismatch at the boundary. We applied this technique in the analysis of the role of corner holes in the formation and the stabilization processes of the 7×7 DAS structure.

In this paper, we present the results of structural analysis performed on quenched and HBO_2-irradiated Si(111) surfaces. We used HBO_2 molecules as adsorbates because of the fact that they preferentially react with the center adatoms in unfaulted half units,[7,12,13)] making it possible to analyze the stability of stacking fault structures during the breakdown process of the 7×7 structure.

2. Experiments

Phosphorus-doped n-type Si(111) ($\rho = 0.4$–$1\ \Omega \cdot$ cm) substrates were used in this study. The samples were chemically

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cleaned by acetone, and then loaded into the UHV chamber. The samples were outgassed at ∼500°C for 12h and then flashed at about 1150°C in order to form the 7 × 7 structure. For the quenching experiments, after confirming the formation of the clean 7 × 7 structure by STM, samples were reheated to ∼1200°C, and then quenched by turning off the heating power. On the other hand, for the experiments with HBO_2 molecular irradiation, after confirming the formation of the clean 7 × 7 structure, HBO_2 molecules were irradiated onto the surface. The entire irradiation process was performed by maintaining the substrate temperature at ∼750°C in order to prevent oxygen incorporation. The HBO_2 cell temperature during irradiation was maintained at ∼800°C.

All STM observations were performed at room temperature using an electrochemically etched tungsten tip. The base pressure was $\sim 1 \times 10^{-10}$ Torr and the pressure during HBO_2 irradiation was less than 2×10^{-8} Torr.

3. Results and Discussion

3.1 STM images of quenched and HBO_2-irradiated Si(111) surfaces

Figure 1 shows the STM images of Si(111) surfaces after (a) quenching (sample bias: $V_s = 2.0$ V, tunneling current: $I_t = 0.3$ nA) and (b) HBO_2 irradiation ($V_s = 2.1$ V, $I_t = 0.45$ nA). The 7 × 7 and disordered structures are observed on each surface. In the disordered structure of the quenched Si(111) surface, there exist domains consisting of c(2 × 8) and other structures as shown in Fig. 1(a). On the other hand, short-range ordering of adatoms forming ($\sqrt{3} \times \sqrt{3}$)R30°, 2 × 2 and c(2 × 4) structures are observed in the disordered structure on the HBO_2-irradiated Si(111) surface (Fig. 1(b)). The difference between the atomic arrangement of the disordered structures on the quenched and HBO_2-irradiated surfaces is due to the difference in their origins. In the case of the quenched Si(111) surface, STM images show a snapshot during the formation process of the 7 × 7 DAS structure. Therefore, the quenched Si(111) surface yields information about the formation process of the DAS structure. On the other hand, the STM images obtained for the HBO_2-irradiated Si(111) surface show the destruction process of the 7×7 structure induced by HBO_2 irradiation. In this process, B atoms are considered to disturb the stability of the DAS structure, and induce the change into the disordered structure.[14)]

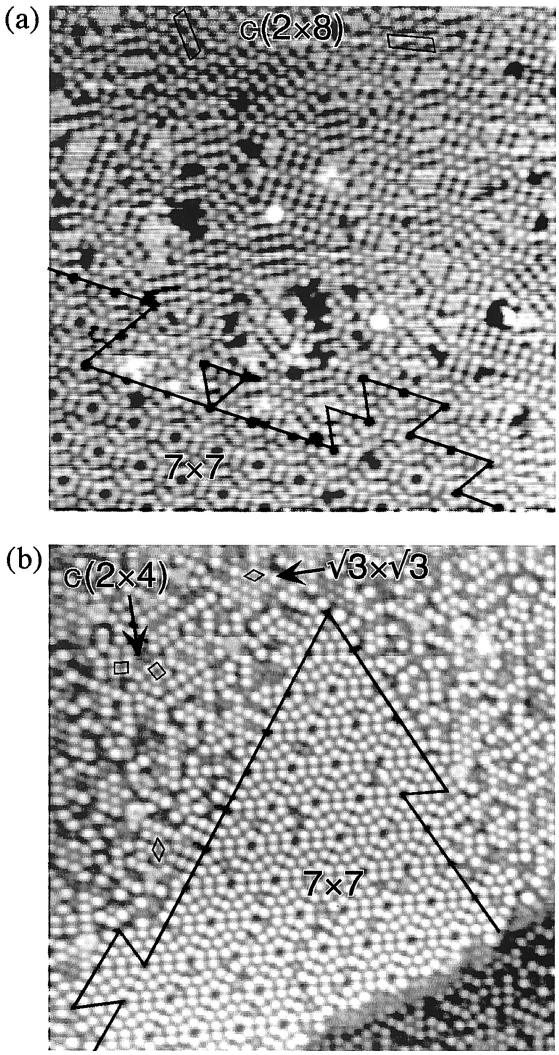

Fig. 1. STM images of the Si(111) surfaces after (a) quenching (sample bias: $V_s = 2.0$ V, tunneling current: $I_t = 0.3$ nA) and (b) HBO_2 irradiation ($V_s = 2.1$ V, $I_t = 0.45$ nA).

3.2 Structural analysis model including underlying layers

Prior to the detailed discussion about the quenched and HBO_2-irradiated Si(111) surfaces, we illustrate the structural analysis model of a simple Si(111) structure. Figure 2 shows the schematics of Si(111) surface structures with (a) and without (b) the stacking fault in the underlying layer. In Figs. 2(a) and 2(b), the large circles, closed circles and closed ellipses correspond to the adatoms, rest atoms, and dimers, respectively, as shown in the inset. In the case of the Si(111)-7 × 7 structure, electrons transfer from the dangling bond state of top-layer adatoms to that of the rest atoms in the underlying layer. The quantity of transferred charge on the adatoms depends on the number of rest atoms that surround the adatoms.[8,9)] By using these characteristic properties of Si(111)-7 × 7 structure, we can analyze the atomic arrangement in the second and third layers of the DAS structure. As shown in Figs. 2(a) and 2(b), the arrangement of adatoms is the same in both cases, however, the stacking fault structure is formed only in the case of Fig. 2(a). This structural

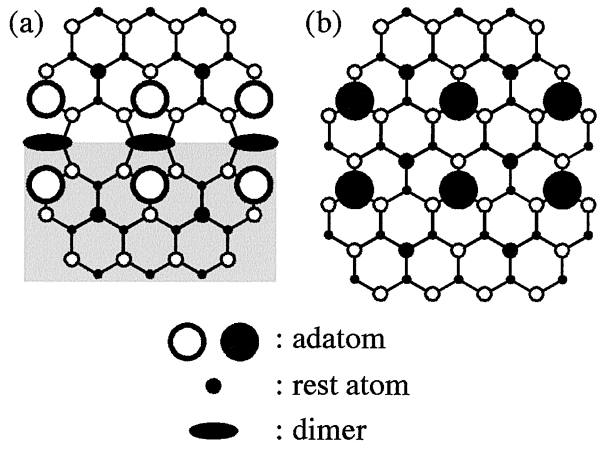

Fig. 2. Schematics of Si(111) surface structure (a) with and (b) without the stacking fault in the underlying layer. The large circles, closed circles and closed ellipses correspond to the adatoms, rest atoms, and dimers, respectively. Gray and white adatoms are considered to become dark and bright, respectively in the filled-state STM image.

difference changes the number of rest atoms surrounding the adatoms. In the case of the normal stacking structure shown in Fig. 2(b), four rest atoms exist around one adatom. On the other hand, when the stacking fault structure exists in the underlying layer, dimers are formed at the boundary between unfaulted and faulted regions as shown in Fig. 2(a). The number of rest atoms surrounding an adatom is reduced as a result of the dimer formation, that is, two rest atoms exist around one adatom. Therefore, the adatoms on the underlying layer with normal stacking structure have less charge density than those on the underlying layer with stacking fault structure. As a result, the adatoms on the underlying layer with normal stacking structure become dark in the filled-state STM image, while the brightness of adatoms does not change for the cas with stacking fault structure. Therefore, we can analyze the underlying layer structures by using bias-dependent STM images.

In the following sections, we analyze the quenched and HBO_2-irradiated Si(111) surfaces in detail by using the technique described above. From the viewpoint described in the introduction, we focus on the role of corner holes in the formation and the stabilization processes of the DAS structure.

3.3 Analysis of the quenched Si(111) surface

On the quenched Si(111) surface, corner holes clearly exist along the boundaries between the 7×7 and disordered areas, as previously pointed out.[7] We analyzed the boundary structures using the structural analysis model proposed by us.[10,11] Figure 3 shows a filled-state STM image ($V_s = -2.0$ V, $I_t = 0.3$ nA) of a boundary region between 7×7 and disordered structures. The adatoms of the corner holes are bright even in the filled-state image as shown in Fig. 3. On the basis of the structural analysis model, these corner holes are surrounded by complete stacking fault and dimer structures; charge transfer is suppressed by the formation of underlying layers.

DAS fragments, which consist of some half units of DAS structures, were also observed in the disordered area as shown in Fig. 4(a). From the same analysis, a stacking fault structure is determined to be formed under these half units. In addition, they share the same corner hole. These results strongly suggest that corner holes with complete stacking fault and dimer structures in the second layer (complete corner holes) play an important role in the formation process of DAS structures. Energetic analysis of the DAS formation process in a subunit level is discussed elsewhere.[15]

On the quenched Si(111) surface, there exist a large number of corner-hole-like structures in the disordered area, as indicated by circles in Fig. 4(a) ($V_s = 2.0$ V, $I_t = 0.3$ nA). A magnified image of this structure and its schematic model are shown in Figs. 4(b) and 4(c), respectively. These figures clearly show that the corner-hole-like structures exist at the boundary of three out-of-phase c(2×8) domains. This result suggests the possible formation mechanism of corner

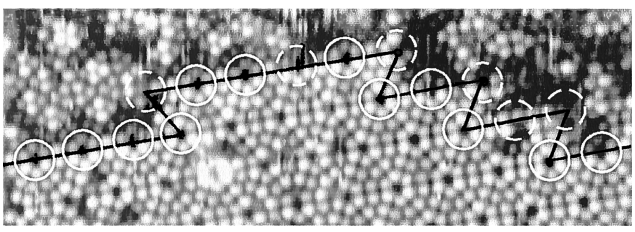

Fig. 3. Filled-state STM image ($V_s = -2.0$ V, $I_t = 0.3$ nA) of a boundary region between 7×7 and disordered structure on a quenched Si(111) surface. The solid and dashed circles indicate the complete and incomplete corner holes, respectively.

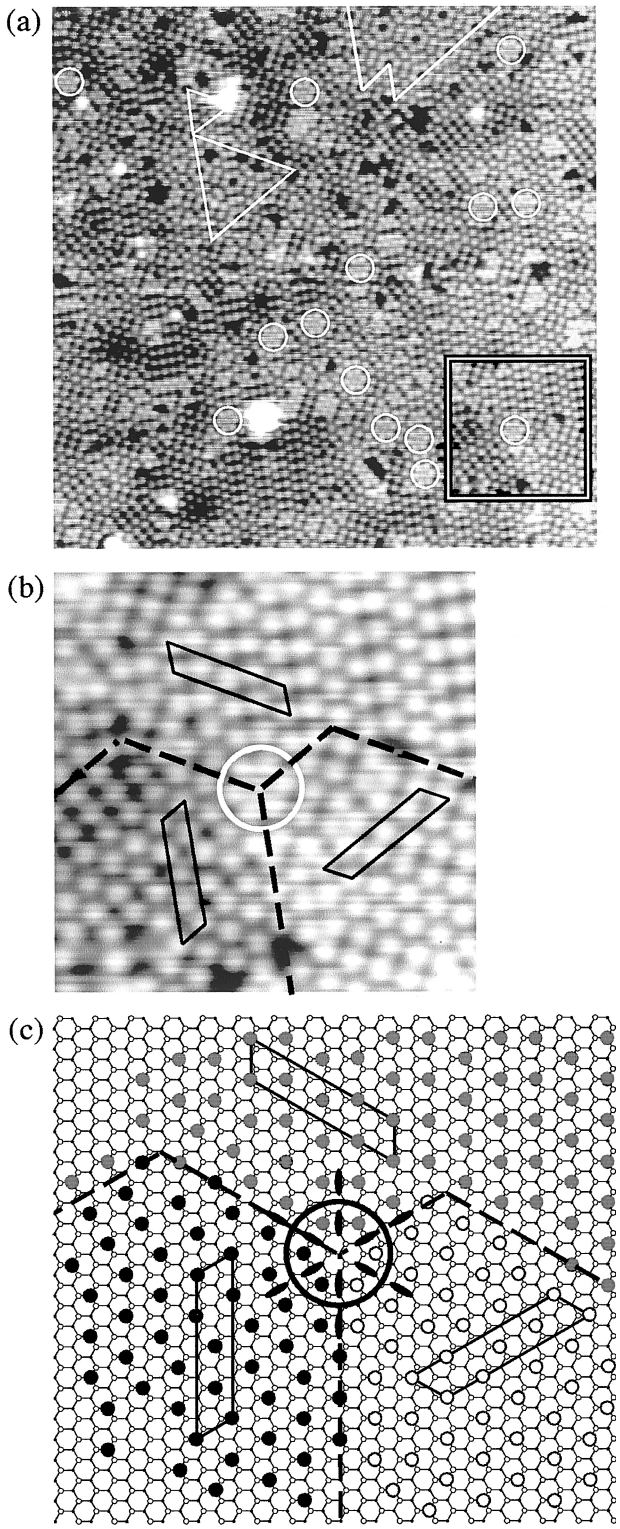

Fig. 4. (a) STM image of a quenched Si(111) surface ($V_s = 2.0$ V, $I_t = 0.3$ nA). (b) Magnification of the corner-hole-like structure indicated by the square in (a). (c) Schematic structure of (b).

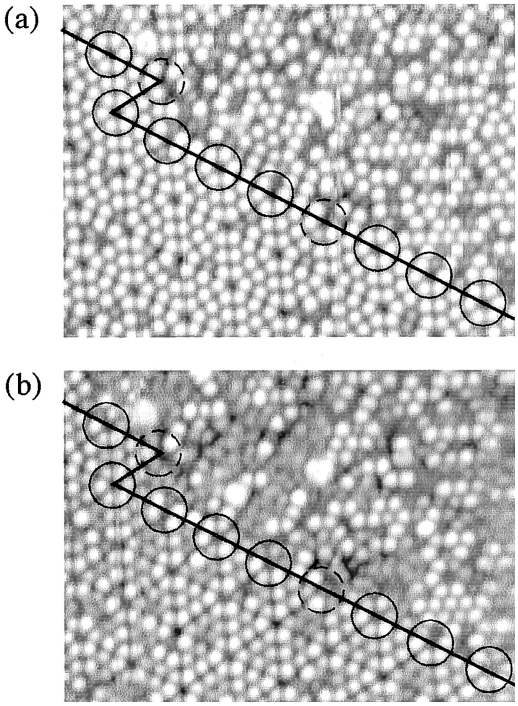

Fig. 5. (a) Empty- (V_s = 2.1 V, I_t = 0.45 nA) and (b) filled- (V_s = −2.1 V, I_t = 0.45 nA) state STM images of the boundary between 7 × 7 and disordered structure on a HBO_2-irradiated Si(111) surface. The solid and dashed circles indicate the complete and incomplete corner holes, respectively.

holes, namely, the nucleation of corner holes may occur at the boundary of the three out-of-phase c(2 × 8) domains. The c(2 × 8) local ordering in the disordered region is formed by simple adatom arrangement with the c(2×8) ordering over the rest atom layer, and does not intrinsically include the stacking fault structures.[6] However, the strain induced by the domain boundary may act as a trigger for the introduction of dimers and stacking fault structures to form complete corner holes.

3.4 Analysis of the HBO_2-irradiated Si(111) surface

In the disordered structure formed on the HBO_2-irradiated Si(111) surface, there exist local atomic arrangements of $(\sqrt{3} \times \sqrt{3})$R30°, 2 × 2, and c(2 × 4) structures. In a previous study, we analyzed their origin, and confirmed that the disordered structure is an intrinsic part of the B-induced reconstruction.[14] Namely, the shorter B-Si bond length increases the tensile stress in the surface layers, resulting in the disturbance of the stability of the DAS structure.[14] In fact, in the case of the HBO_2 molecular irradiation, there exist no corner-hole-like structures and DAS fragments that were observed in the case of the quenched surface as shown in Fig. 1(b).

Figures 5(a) and 5(b) show empty- (V_s = 2.1 V, I_t = 0.45 nA) and filled-state (V_s = −2.1 V, I_t = 0.45 nA) STM images. It is clear that corner holes exist along the boundary between the 7 × 7 and disordered area as in the case of the quenched surface. The adatoms surrounding the corner holes which exist along the boundary are bright even in the filled-state STM image (Fig. 5(b)). This result indicates that the complete stacking fault and dimer structures are formed in the second layer. Namely, the complete corner holes play an important role not only in the formation process but also in the stability of the 7 × 7 structure.

4. Conclusions

Bias-dependent STM images of the quenched and HBO_2-molecule-irradiated Si(111) surfaces showed that the complete stacking fault and dimer structures are formed in the second layer around the corner holes existing along the boundary between 7 × 7 and disordered structures. This result indicates that the complete corner holes play an important role in both the formation and the stabilization processes of 7 × 7 DAS reconstruction. In addition, the formation of a structure similar to a corner hole was often observed at boundaries of three out-of-phase c(2 × 8) structural domains in a quenched surface, which may be a nucleus for the formation of corner holes.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

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